

An ASTM Approach to the Standardization
of New Techniques for Coal Analysis

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ASTM Committee D-5 on Coal and Coke is responsible for development of specifications for coal and for coke produced from coal; the development of methods of sampling, analysis, and testing; the development of specifications for classification of coals on the basis of chemical and physical characteristics; the standardization of terminology; and the promotion of research and dissemination of knowledge in these fields. The work of the committee is co-ordinated with other ASTM committees and other organizations having common interests.

The committee is made up of producers, users and those whose general interests are in coal as a resource and its utilization. The standards produced by the committee reflect this balance of membership. To ensure that standards are kept up-to-date in the opinion of those who use them, the Society dictates that all standards must be reviewed every five years and, if they are neither reapproved nor revised, they must be withdrawn as standards. To further ensure that modern standards are available when required, an ad hoc task group is appointed by the committee at regular intervals to study existing standards, to critically evaluate them in the light of current usage and to recommend the needed changes. The task group may also suggest the standardization of tests necessary to coal-conversion processes such as gasification and liquefaction.

ASTM Standards for coal and coke have never been static, nor are they considered to be the last word; they are, however, the best available at the time. Revisions to existing methods are made frequently within the five-year review period. All revisions other than those of an editorial nature must be approved by letter ballot of the committee before they are accepted.

Analytical procedures for coal and coke may be divided into two groups: those based on empirical methods developed in the early years of this century, and those based on stoichiometric chemical reactions. Empirical test methods, such as moisture, ash and volatile matter, were developed in the industry to fulfil a commercial need and finally they became standards. These tests remain much the same today as when they were adopted 60 or 70 years ago. Using these tests, a considerable bank of data has been accumulated, which can be compared with current analyses carried out by essentially the same methods.

On the other hand Standard methods based on stoichiometric reactions have progressed rapidly in the past 10 to 15 years. Ash analysis, i.e. mineral analysis of coal and coke ash for the ten major constituents, has progressed from the time-consuming wet chemical procedures, through a combination of wet chemical, flame-photometric, and spectrophotometric methods which resulted in the adoption of D 2795 in 1969. The latest editorial revision was in 1975. In the intervening time it was realized that better and less time-consuming methods were available and work is well advanced in developing an atomic-absorption procedure using a lithium tetra-borate fusion technique. The new method has good precision and can be carried out with relative speed. One of the major difficulties in this program has been the lack of standard reference samples for the major elements present in coal ash. Standard

Reference Materials for total sulfur in coal, mercury in coal and fly-ash and several other trace elements in coal and coal ash have been available for some time from the National Bureau of Standards. Steps are being taken to request NBS to prepare Standard Reference Materials for the major elements in coal and coal ash.

Concern with the environment and laws governing the levels of allowable pollution from the use of coal have prompted the standardization of analytical methods for the determination of these pollutants. Many analytical methods have been developed by governmental agencies and universities, using a wide range of techniques. The task of filtering out the best and most practical methods with reference to coal has fallen on Committee D-5. Many of the proposed methods require expensive and highly sophisticated instrumentation. We in ASTM feel that an acceptable standard method must be within the financial reach of those expected to use it. Very few laboratories have the capabilities of carrying out certain test methods because of the high cost of instrumentation. Atomic absorption spectrometry is now considered quite common on this continent, and is no longer considered exotic. The principles are well established and most laboratories have operating experience. On this assumption we feel justified in standardizing methods using this approach. We still have reservations when it comes to the standardization of methods based on X-ray fluorescence (XRF), neutron activation etc. There is no doubt that these methods will be acceptable in the near future as techniques improve and the costs come within the reach of commercial laboratories.

Many new techniques have been suggested for coal analysis; one is the micro-determination of carbon and hydrogen which has proven to be a valuable tool in research where the amount of sample may be limited to a few milligrams. The micro method requires that the sample weight be in the order of 10 milligrams. To extract a representative sample of that size from a laboratory sample of coal (-0.250mm, #60 U.S. Standard Sieve or even -0.074mm, #200 U.S. Standard Sieve) is difficult if not impossible. A semi-micro technique can probably be developed. However the Liebig method as described in D 3178 will suffice until a new method is developed.

A semi-micro method for the determination of nitrogen in coal is being studied at present. As this procedure is faster than the Kjeldahl method, requires less space and is less costly, it is likely to receive early acceptance as an alternative to D 3179.

Many methods have been proposed for the determination of sulfur in coal and coke, and to-date only a few have been found suitable for standardization. The basic method with which all methods are ultimately compared is the Eschka Method. The Bomb-washing and the High-temperature-combustion methods are acceptable alternatives. Combustion methods, using induction or glow-bar-heated furnaces to convert the sulfur compounds to SO_2 , have been examined and found to be unsuitable as standard methods. It is reported that newer designs of this type of equipment are much more reliable. Experience indicates that frequent standardization against analysed standards is advisable.

Also with reference to sulfur determinations, improvements have been incorporated in the method of determining pyritic sulfur in coal. In the present method, D 2492 Forms of Sulfur, pyritic sulfur is determined by extracting a weighed sample of coal with dilute nitric acid followed by a titrametric determination of iron as a measure of pyritic sulfur. Appropriate corrections are made for non-pyritic iron.

As an alternative procedure the pyritic iron may be determined by atomic absorption.

Over the years D-5 has been presented with the problem of developing a standard to cover coal stockpile inventory which is of concern to utilities and other large users of coal. This task has been carried out for years by time-consuming

measurement of the pile to determine its volume as accurately as possible followed by an also-time-consuming sampling program to determine the average density of the coal at varying depths in the pile. From these measurements, which were rough at best, the tonnage was calculated. We have now been asked by CAPCO (Central Area Power Coordinating) Group, to co-operate in their program to develop a standard. This group, some of whose members are from D-5, are studying the feasibility of the use of a nuclear probe and scaler which would operate on the basis of gamma radiation and reflection to accomplish the required measurements. A second approach under consideration is the use of a radio-echo device. D-5 cannot participate directly in the development stages but will be interested in standardization when the necessary instrumentation is developed.

D-5 has an ash analysis standard, and a standard method for the preparation of ash. We have now been requested to develop a method for the preparation of an ash (fly-ash) which is non-standard, to simulate ash produced under pulverized fuel burning conditions. Ash produced under such conditions would be vastly different from that prepared under the standard conditions specified in D 2795, i.e. from room temperature to 500°C in one hour and 750°C in two hours, and finally ignited to constant weight at 750°C in a well-ventilated muffle furnace. Ash produced under the conditions prevailing in a pulverized fuel burning system would be subjected to much higher temperatures, thus causing the volatilization of elements such as sodium. It is also true that some of these volatile constituents may recombine to varying degrees, producing compounds not normally found in the standard ash. A group on the west coast has asked for our co-operation in this project, which will involve the ashing of a relatively large sample of coal under specific conditions. The specific conditions necessitate the use of a specially designed mini-furnace to burn the coal in a pulverized form to produce the simulated ash. The design and construction of the furnace will be undertaken by this group.

The group representing utilities and manufacturers of electrostatic precipitators require an ash prepared in this manner so that, when a chemical analysis, resistivity measurements and other tests are made, the data so obtained can be correlated with the ash (fly-ash) present in the stack from which they are attempting to remove the particulate emissions. An ash prepared by conventional standard methods does not meet these requirements.

Fuel calorimeters manufactured today are highly sophisticated as compared to those in use in the thirties. While thermometers may still be used to measure temperature-rise they have in many instances been made superfluous by the introduction of thermistors. Most modern adiabatic calorimeters have both, thermometers manufactured to ASTM standards and thermistors with digital read-out, and in some instances a print-out attachment is added. The use of this modern instrumentation, while not sanctioned by ASTM, is found to be very satisfactory in helping to eliminate the human element.

The manual operation of the cold - and hot-water valves in an adiabatic calorimeter has been superseded by automatic operation. This new instrumentation is good and exceedingly reliable.

The determination of volatile matter in coal and coke can now be carried out in duplicate, using equipment programmed to lower the crucibles into the furnaces at the required rate, to hold them there for a given time and then to withdraw them.

While many of the methods have remained basically the same for many years, automation has assisted the analyst to turn out more work with precision equal to or greater than that with the manual methods.

In conclusion it should be pointed out that D-5 is not against the use of new technology in the preparation of standards but, by the time the technology has been advanced and proven reliable, it is no longer new. To be considered worthy of standardization a new approach must be faster than the one it is to replace, must have equal or greater precision, and the equipment required must be within the reach of the laboratories who will be expected to use it.